Electro-optic Properties of Siloxane Based Liquid Crystal Polymers

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Abstract

A series of siloxane based side chain liquid crystal polymers have been prepared with a systematic variation in spacer length. All the polymer exhibited a smectic phase, for which the smectic-isotropic transition temperature increased as the spacer length increased. Infrared dichroism and x-ray scattering procedures have been utilized to determine the orientational order parameters for this series of polymers and these are related to the measured electrooptical properties. It is found that with increasing spacer length (n) of polymer the threshold voltage is lowered with a functional from of n^{-2} and that the variation of the threshold voltage arises from changes to the intrinsic curvature elasticity rather than to differences in orientational order. A simple model is used to indicate the origion of the effects observed which appear to arise from the constraints offered by the coupling of the mesogenic units to the polymer backbone.

الخلاصة

تم تحضير سلسلة من البوليمرات السايلوكسانية تختلف عن بعضها البعض بتغير طول الفاصل ، كافة هذه البوليمرات أظهرت الطور السمكتي و أن درجة حرارة الطور السمكتي إلى الايزوتروبي تزداد مع زيادة طول الفاصل. تم استخدام طريقة التلونية لاشعة تحت الحمراء و تشتت الأشعة السينية لأيجاد عامل الاتجاهية للبوليمرات وتم توضيح علاقتها بالخصائص الكهروبصرية المقاسة . وجد انه بزيادة طول الفاصل(n)للبوليمر يؤدي الى خفض فولتية العتبة و بدلالة (n^{-2})و ان التغير الحاصل بفولتية العتبة يؤدي إلى التغير الحاصل في معامل المطاطية و كذلك اختلاف عامل الاتجاهية. تم استخدام موديل ليوضح أصل هذه الظواهر و التي تنشأ بسبب قوة الربط بين المجموعة النهائية للبوليمر إلى عموده الفقري بواسطة الفاصل.

Introduction

Side chain liquid crystal polymers are a composite from of macromolecule built up from three basic types of molecular unit. These are the polymer backbone, the mesogenic units, and the coupling chains which link the mesogenic unit to the polymer chain. A large number of side-chain polymers in which the nature of these three components and their interconnection are varied have been synthesised and studied [1,2]. Fundamental to understanding such materials is a quantitative knowledge of the interactions between those three normally incompatible components for which the inherent connectivity of the polymer system inhibits large scale segregation. It is now clear that the relatively short length of coupling chains will result in some interaction between the mesogenic unit and the polymer backbone chains. A variety of nematic phases have been proposed [3,4], in which the sign of the coupling may favour a positive or parallel arrangement simply because of the nematic field, or the bias may be to a perpendicular

or negative arrangement of the side group and the polymer chain due to the particular geometry of the coupling chain. Small angle neutron scattering experiments have shown that for polyacrylate and polysiloxane based side chain liquid crystal polymers both positive [5] and negative coupling [6] are possible, although the level of coupling in either case is relatively small. Studied involving cross-linked systems [7] and fibres [8] have shown that there is a regular alternation in the sign of the coupling for a particular polyacrylate and polysiloxane based systems as the length of the coupling chain is increased. This contribution focuses on the influence of this coupling between the mesogenic side-group and the polymer backbone on the resultant electro-optic properties of such materials. In particular we centre our attention on the influence of the coupling chain upon the curvature elasticity which determines the ease with which the director pattern may be modified using external electric fields . A number of contributions concerned with these properties have appeared, for example [9,11] although none has considered the systematic variation of properties with changing coupling chain length for a series of polymers. We shall considered a series of polysiloxane based side-chain liquid crystal homopolymers in which the coupling chain length is systematically varied. The state of orientational in these homopolymers is obtained through the use of infra-red spectroscopy and x-ray scattering techniques. Carefully programmed electro-optic measurements are used to evaluate the threshold voltages for this series of polymers. Comparsion is made with existing models of curvature deformation in low molar mass liquid crystal systems.

Experimental

An electro-optic experiment involves the measurement of changes in the optical properties of thin film of liquid crystal polymer induced through the application of an electric field. The experimental arrangement used for these electro-optic cell (described below) was held inside a temperature controlled stage providing a uniform temperature environment within fluctuations of 0.25 ^{0}C. The optical system consisted of a 5mW helium-neon laser with crossed polarizer and analyzer configuration and a photodiode with amplifier for light intensity measurements. Electric fields were provided by means of a power amplifier (HP 6827A) driven by a function generator (Thandar TG501), an arrangement which could provide waveforms in the frequency rang 0.05 to 30 KHz with peak to peak voltages in the range 0 to 240 volts. In this study a fixed frequency of 500 Hz was used throughout. The intensity of transmitted light through this optical system was recorded as a function of time using a microcomputer system based around an IBM compatible PC. Through the use of a specially written software system,EOCS, sophisticated electo-optical experiments could be performed on a continuous or cyclic basis, involving temperature control, data recording, field switching and analysis [17]. Electro-optic cells with predefined director orientation were constructed from patterned tin oxide coated glass slides (Baltracon Z20). The cell electrodes, after cleaning in an ultrasonic bath and drying, were coated with a thin layer of a polyimide precursor consisting of a 5% solution of Rodehftal 322 in dimethylformamide using a spin coater. These coated slides were then subjected to thermal cycles and a mechanical treatment using a cloth. The selected polymer sample was carefully

applied onto one of the treated glass electrodes and the complete assembly was heated above the clearing point of the polymer in order to allow the trapped air to escape. The second glass electrode was then mounted above the first electrode using 0.025 mm thickness Kapton sheet as spacers . The quality of the prealignment treatment was confirmed through examination of each cell with a polarizing microscope. Complete and uniform director alignment was obtained by holding the completed electro-optic cell at a temperature 1 ^{0}C below the measured clearing point for 10-24 hours. This technique was successful in inducting a uniform director alignment within the electro-optic cells prepared for all the materials used in this work. In all cases the predefined director alignment was parallel to the electrode surface and to the direction of rubbing.

The orientational order parameter S for the polymers in the series with n=4,5,6 was measured as a function of temperature using infra-red dichroism employing a Perkin-Elmer 580B spectrometer fitted with a wire grid polarizer and heating stage [18]. The order parameter measurements were made at a variety of temperatures using monodomain samples prepared as prealigned cells similar to those used for the electro-optic measurements but using crystals of potassium bromide as the cell windows [18]. For each measurement care was taken that the prealigned cell had sufficient time to reach equilibrium and successive measurements over a time period were taken to ensure this was the case. The orientational order parameter for the polymer CBZ3 was measured using x-ray scattering techniques [19,20]. The measurements were made using monodomain samples prepared by holding in a magnetic field (0.6T) at a variety of temperatures. The x-ray scattering measurements were made at room temperature on quenched glassy samples using a computer controlled 3- circle diffractometer [19]. It was not possible to prepare monodomain samples of polymer CBZ2 using either the prealignment on potassium bromide discs or by means of the available magnetic fields. As an alternative approach an estimate of the order parameter as a function of temperature was made by utilizing data obtained from a similar cross-linked liquid crystal system based on a copolymer with n=2 and 4 mol% hydroxyethylacrylate [7]. For this liquid crystal elastomer, monodomain samples can be prepared using a stress field, and the orientation measurements were made using x-ray scattering techniques [19].

Results

Static Electro-Optic Properties

This study is concerned with evaluating the static electro-optic properties for the range of liquid crystal polymers shown in Table 1 as a function of temperature. By using the experimental arrangement described in the previous section it was possible to determine the threshold electric field required to distort the surface prealigned director orientation. For all polymers the dielectric anisotropy is positive. The electric field deforms an initial planar surface alignment and in this case of the geometry is dominated by the splay component of the curvature elasticity K_{11} for small deformations. The threshold voltage U_{th} is related to the curvature elasticity, assuming strong anchoring by [21]:

$$U_{th=} \qquad \sqrt{\frac{K11}{\varepsilon_0 \Delta\varepsilon}} \qquad 1$$

Where $\Delta\varepsilon$ is the anisotropy of the dielectric permittivity, Equation (1) suggests that evaluation of K_{11} should be a relatively straightforward procedure. However for a polymer system there are a number of particular problems involved in the evaluation of U_{th} , each of which relates to the high viscosity of the polymer. The most important of which is ensuring that before starting any measurements the sample is in a complete equilibrium state. For each of the samples considered and for each temperature of measurement we have establish the real relaxation time of the polymer system through the use of a cyclic electro-optic procedure [17,18]. This type of experiment ensures that the relaxation times measured relate to response of the complete system by using a probe, the response time following the application of an electric field [17]. All threshold voltage measurements were made after the sample had been held at required temperature for a period of time at least three times the relaxation time. As the response time following the application of small voltages is particularly long we determined the threshold from a plot of the change in the transmitted optical intensity as a function of the applied small voltage. By extrapolation this method allowed both the true threshold voltage to be estimated and any dynamic effects to be excluded. To ensure that a steady state was reached following each voltage step the sample was left for a period between 3 and 5 hours. During this time the transmitted light intensity was monitored to ensured that the steady state had been achieved. Typically at each stage the sample was held for a period of time ten times longer than the response time.

The threshold voltages obtained in this manner may be related to the curvature elastic constant only if it is valid to assume strong anchoring of the director at the cell wall. The nature of the anchorarge may be assessed by measuring the threshold voltage for a series of equivalent cells with differing cell thicknesses. A plot of the reciprocal of the threshold electric field E_{th} against the cell thickness should be linear and passs through the origion only if the surface anchorage is strong and hence Equation 1 applies. Figure 2 shows the results of such an investigation, this is the case for CBZ6, and it is clear that the conditions for strong anchorage have been met.

Figure 3 shows the experimentally determined threshold voltages for the series of polymers described in Table 1 measured as a function of temperature. It was not possible to make reliable and measurements at temperature lower than those reported in the figure. There is a marked reduction in the threshold voltage for both increasing temperature and spacer length. A similar

trend in terms of the of temperature behavior has been observed in the study of a series of copolymers with n=6 [18]. The increase in the threshold voltage with decreasing spacer length is shown more clearly in figure 4. The variation of the threshold voltage with systematically changing coupling chain length correlates with spares variety of values for similar polysiloxane based polymers reported in the literature [8,22-24].

Discussion

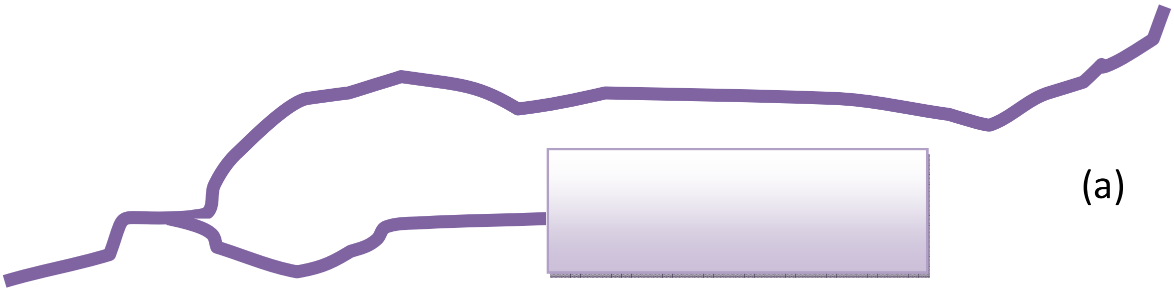
The variation of the coupling chain length in this series of siloxane based side chain liquid crystal polymers has impact upon both the phase behavior and upon the electro-optic properties. The increase in the smectic-isotropic transition temperature with increasing spacer length mirrors similar behavior found in homologous series of low molar mass liquid crystalline materials [15]. In these cases the increase is attributed, at least in a first approach, to the increasing degree of anisotropy of the mesogenic unit. Of course this is also true of side-chain liquid crystal polymers, but for such materials there is the added complications arising from the constraints and interactions provided by the polymer chain. It would be reasonable to assume that as the coupling chain shortened, so the coupling between the mesogenic unit and the polymer chain would increase. If ordering increases as a result of this coupling, it is natural to expect the transitions to rise. In practice as shown in Table 1 the opposite is observed. This suggests that the emphasis on the role of the polymer chain should be one of constraint than enhanced ordering through coupling. Clearly there is a subtle balance between these possibilities and small variation can lead to marked effects. In terms of the variation of the smectic-isotropic , variation transition temperature with spacer length, this appears to have some element of the well-known odd-even effect observed in low molar mass liquid crystalline materials [15] and in main –chain liquid crystal polymers [16]. The increase in the glass transition temperature with decreasing spacer length follows expectations based on the restricted motions of the polymer backbone segments.

Clear trends are observed in the threshold voltage variation as a function of both temperature and spacer length. It is emphasized that considerable care and effort has been taken to exclude from these experiments the time dependent effects of the high viscosities associated with polymeric liquid crystal systems. In part the increase of the threshold voltage with decreasing temperature is expected on the basis of an increasing order parameter. The origin of the variation of the threshold voltage with spacer length is not so clear. If we make any correction for the slight increase in the dielectric anisotropy with decreasing spacer length, then this will simply enhance the rapidly increasing threshold voltage at low values of n. Figure 6 shows that this rapidly rising threshold voltage with changing coupling chain length arises in part from factors beyond those related to the varying order parameter. In the spirit of the approach of Nehring and Saupe [27,28] we may relate this to some increase in the intrinsic curvature elasticity of the system. Of course this type of model only fits the data in the most general way and it is inappropriate to attempt to extract quantitative information from this approach.

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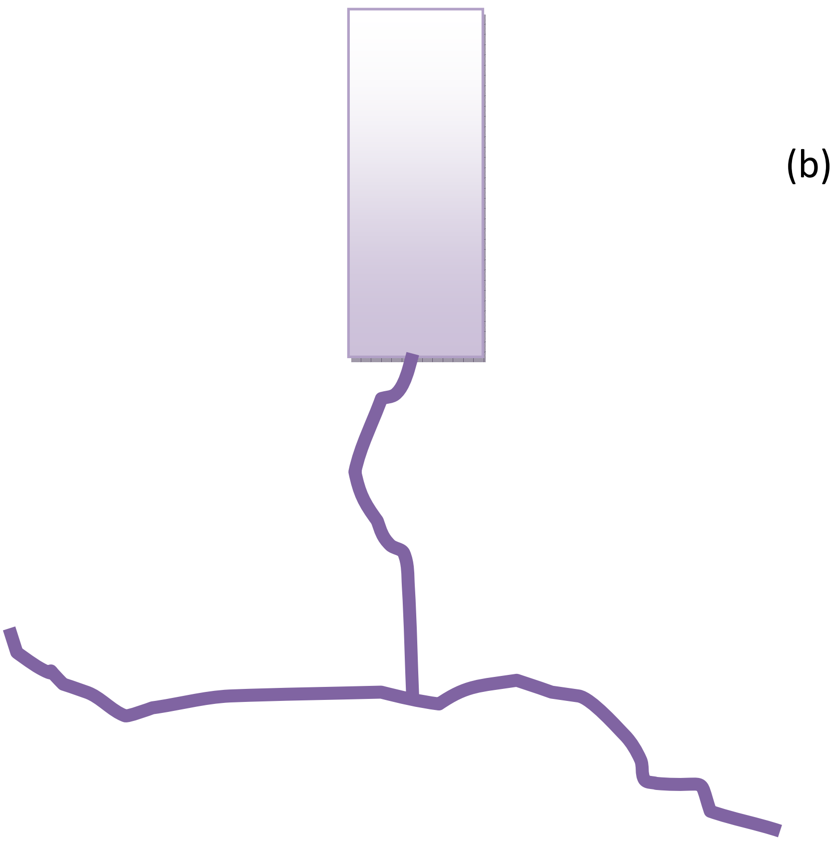
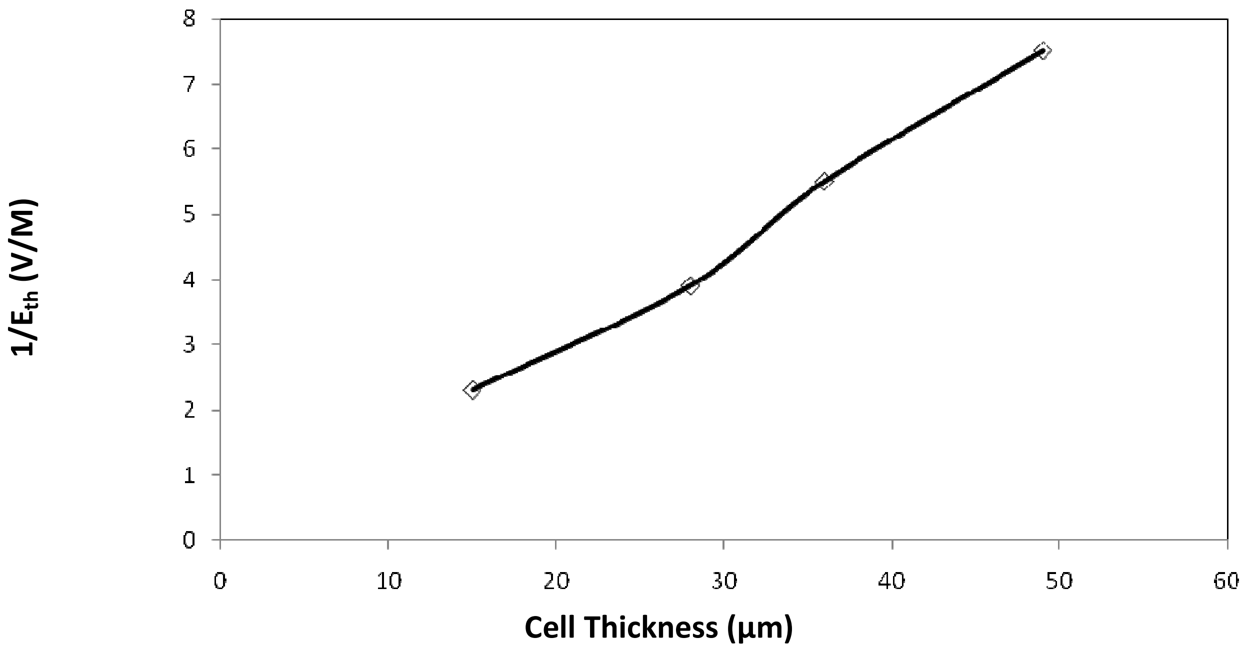
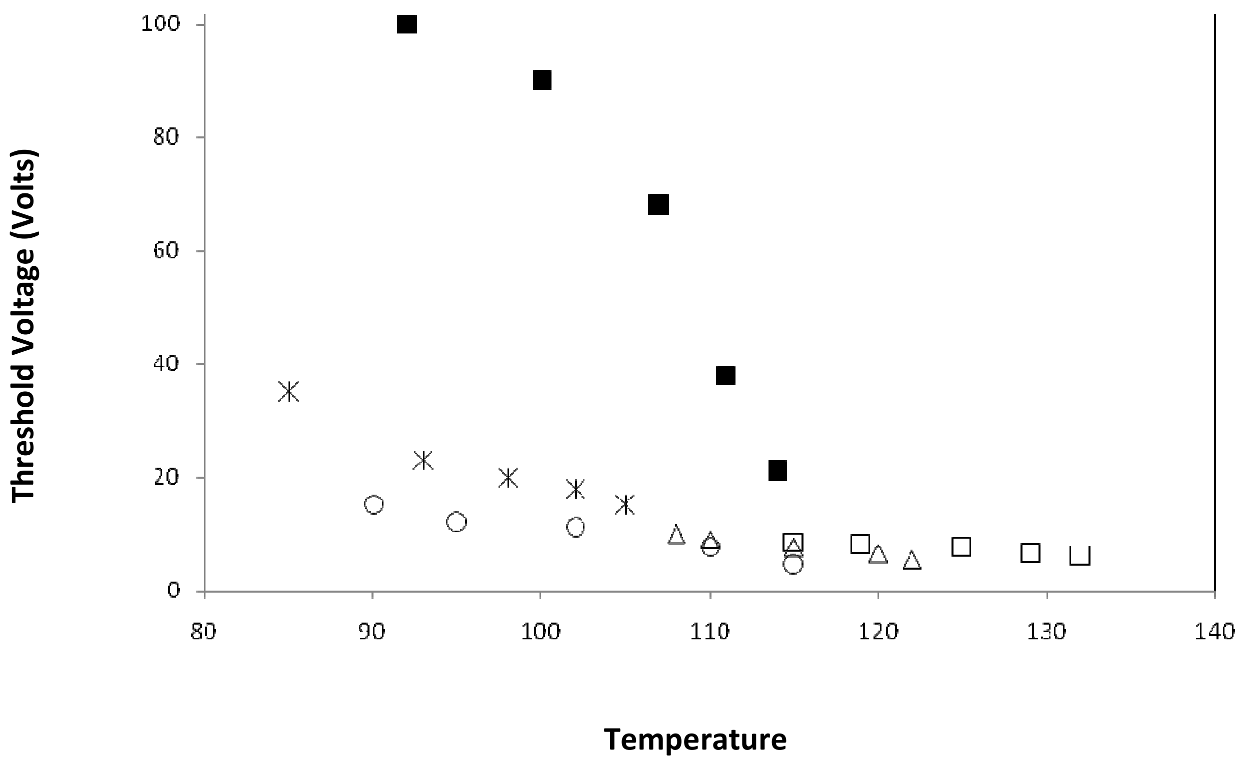


Fig -1 -



8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
1/E_th (V/M)
Cell Thickness (µm)

Fig.2



100
80
60
40
20
0
80
90
100
110
120
130
140
Threshold Voltage (Volts)
Temperature

Fig.3

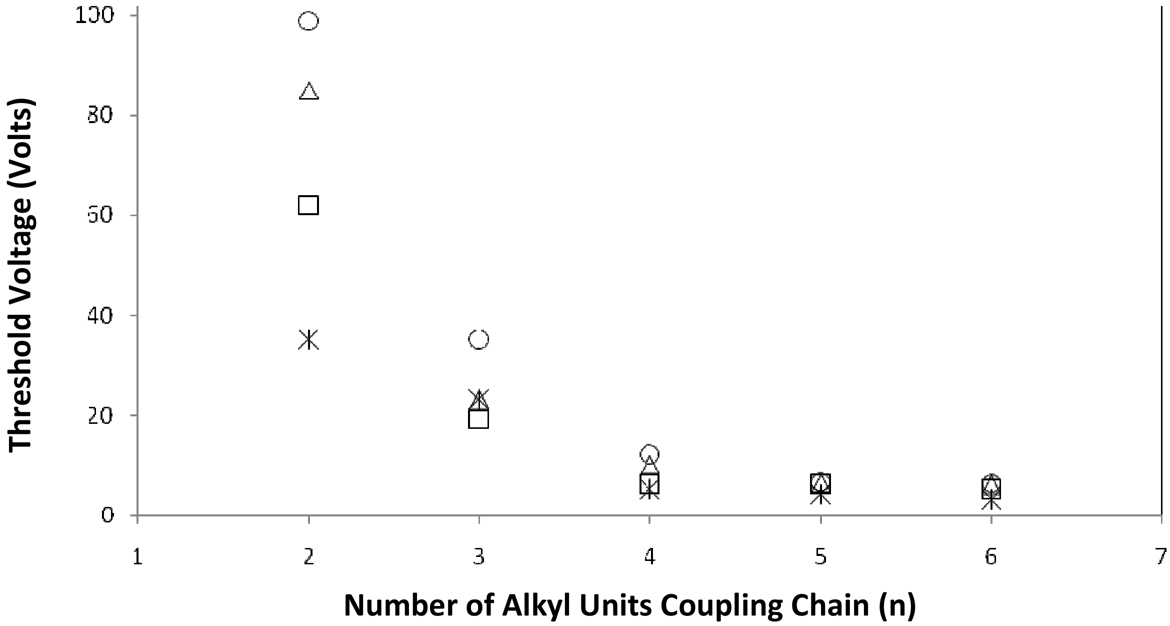

Threshold Voltage (Volts)
Number of Alkyl Units Coupling Chain (n)
100
80
60
40
20
0
1
2
3
4
5
6
7

Fig. 4

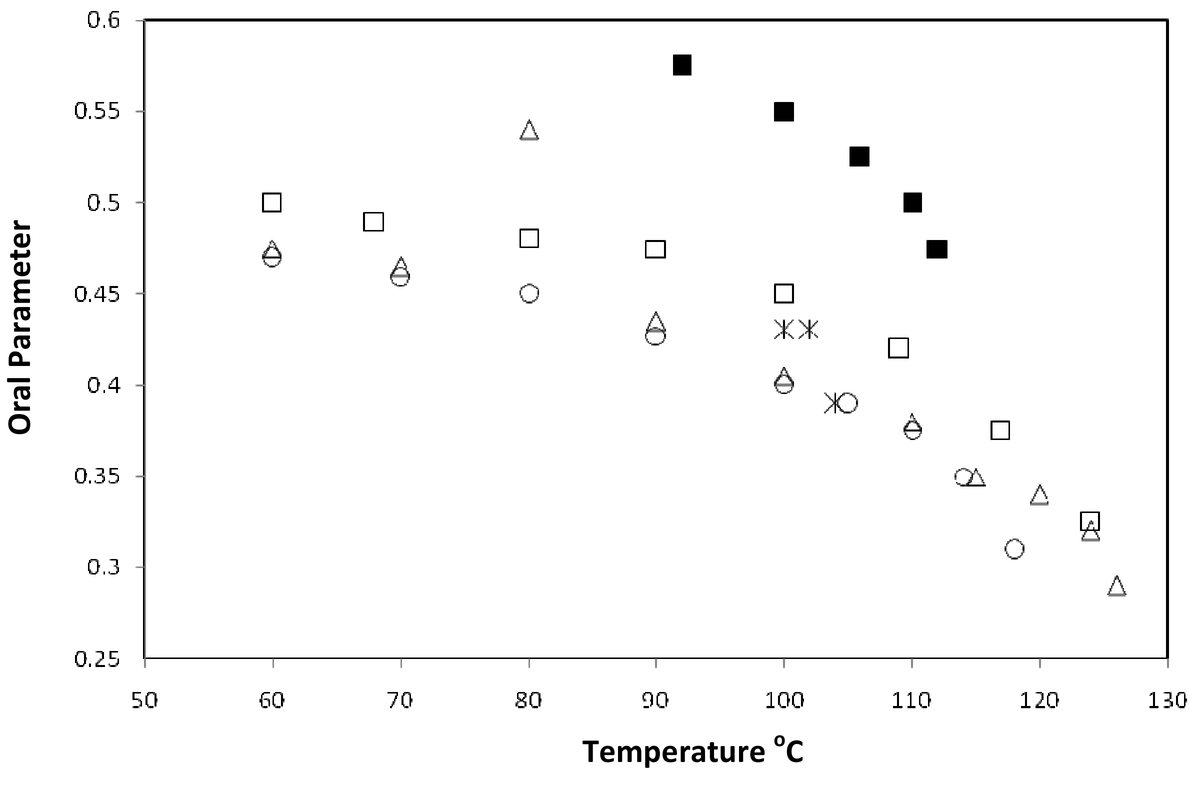
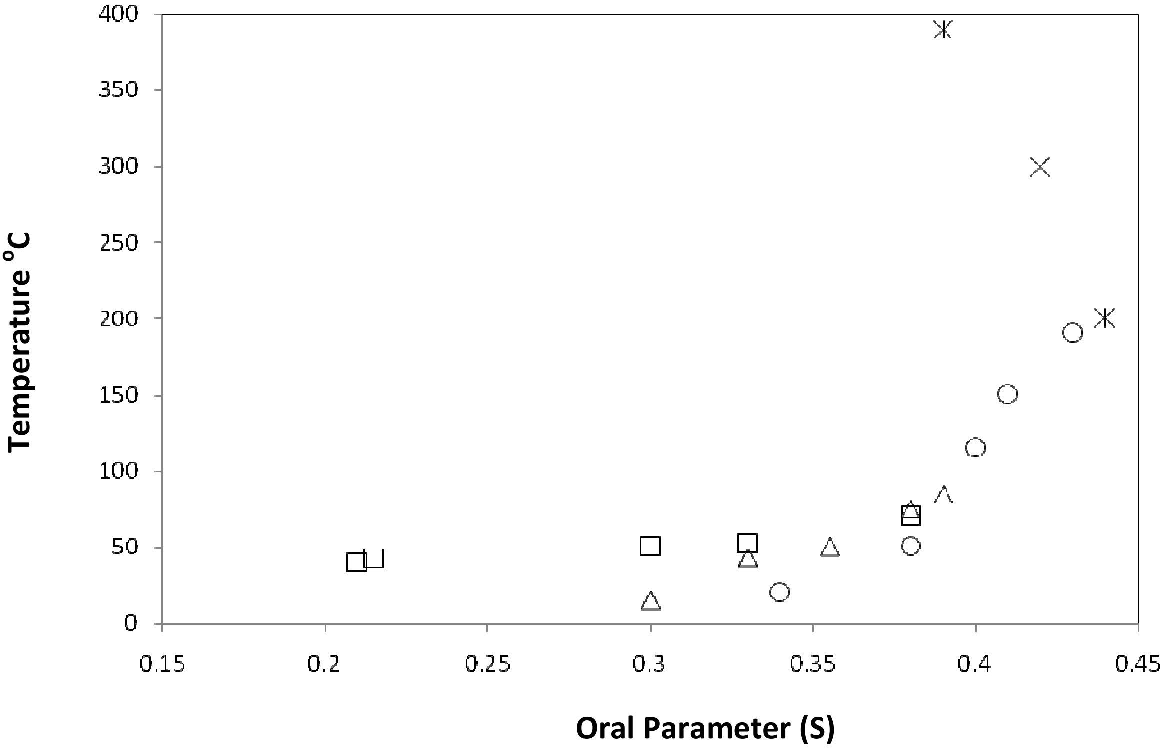
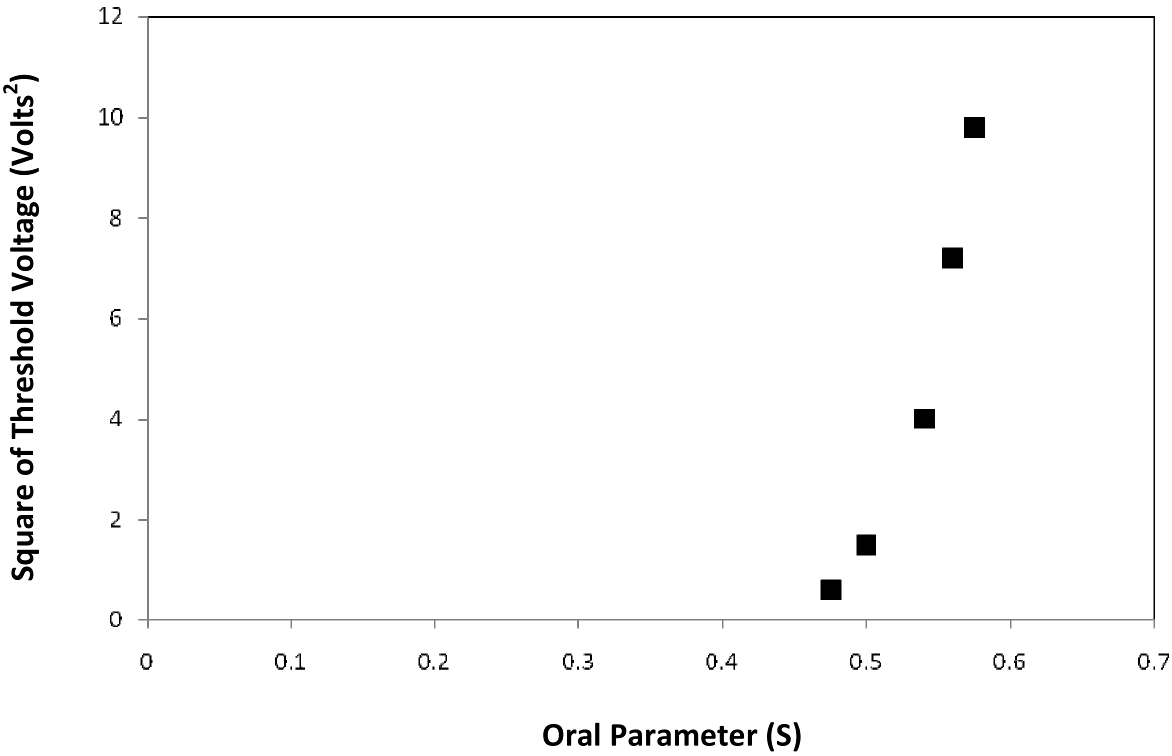

Oral Parameter
Temperature °C
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
50
60
70
80
90
100
110
120
130

Fig.5



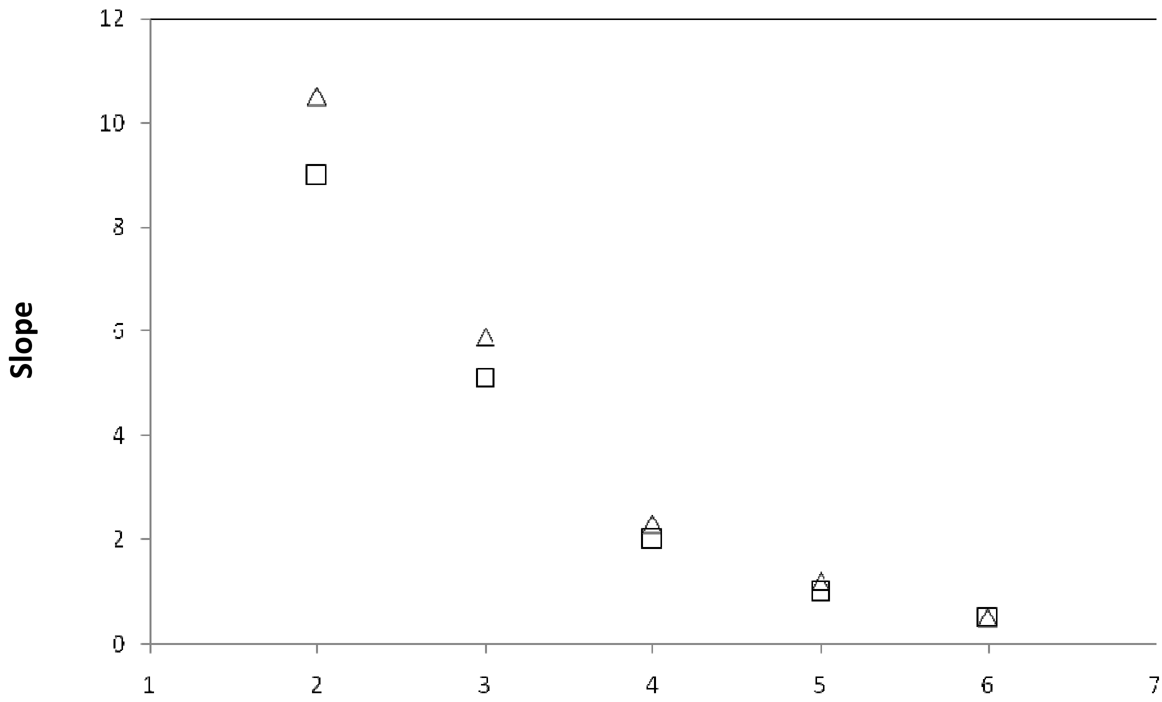
Temperature °C
400
350
300
250
200
150
100
50
0
0.15
0.2
0.25
0.3
0.35
0.4
0.45
Oral Parameter (S)

Fig.6a



Square of Threshold Voltage (Volts²)
12
10
8
6
4
2
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Oral Parameter (S)

Fig.6b



Number of Alky Unit in Coupling Chain (n)

Fig.7

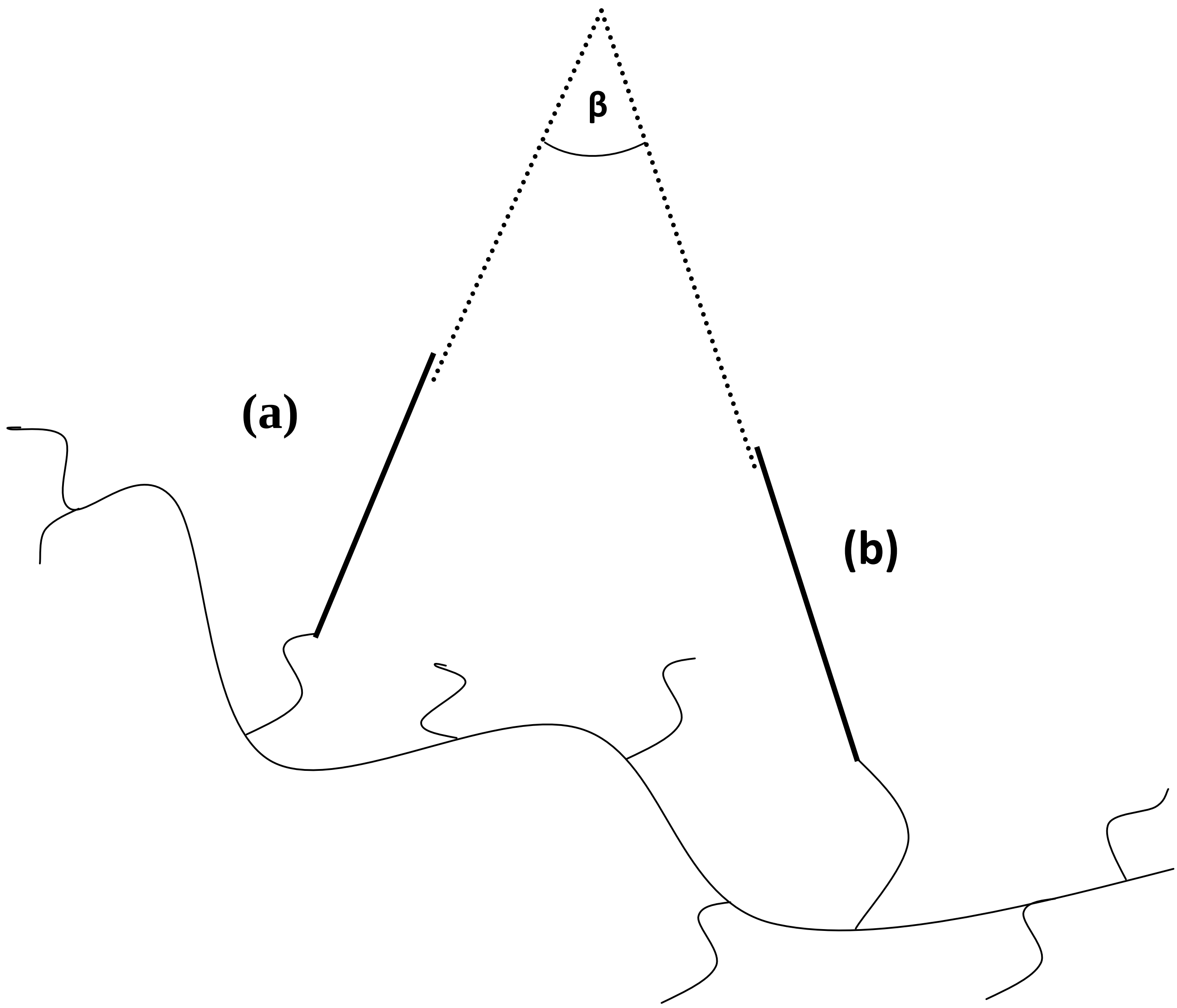


Fig.8